(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 November 2001 (08.11.2001)

PCT

(10) International Publication Number
WO 01/83617 A1

(51) International Patent Classification[7]: C08L 71/12, 77/00, C08K 5/00, C08J 7/04

(21) International Application Number: PCT/US01/40377

(22) International Filing Date: 26 March 2001 (26.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/201,805 4 May 2000 (04.05.2000) US
09/635,041 4 August 2000 (04.08.2000) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/83617 A1

(54) Title: METHOD FOR IMPROVING THE PAINT ADHESION OF COMPATIBILIZED POLYPHENYLENE ETHER-POLYAMIDE COMPOSITIONS

(57) Abstract: Thermoplastic resin composition are provided that comprise a thermoplastic resin and an amount of antioxidant effective to increase the adhesion of paint to an article made from the composition. Also provided are methods to improve the paint adhesion of articles wherein the articles have been subjected to a temperature of at least about 330 °F for period of at least about 10 minutes. In a preferred embodiment, the antioxidant, also known as a stabilizer, or mixture of stabilizers is selected from the group consisting of the phenolic antioxidants, the 3-arylbenzofuranones, the hindered amine stabilizers, the ultraviolet light absorbers, the alkaline metal salts of fatty acids, the hydrotalcites, the epoxydized soybean oils, the haydoxylamines, the tertiary amine oxides, thermal reaction products of tertiary amine oxides, the thiosynergists, and mixture containing at least one of the foregoing.

METHOD FOR IMPROVING THE PAINT ADHESION OF COMPATIBILIZED POLYPHENYLENE ETHER-POLYAMIDE COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/201,805, filed May 4, 2000, which is incorporated herein by reference.

FEDERALLY SPONSORED RESEARCH

Not Applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to methods to increase the paint adhesion of an article made from compatibilized polyphenylene ether-polyamide resin blends.

The invention also relates to the compositions and articles, e.g., automotive components, made from the compositions.

2. Brief Description of the Related Art

Poly(phenylene ether) resins (referred to hereafter as "PPE") are commercially attractive materials because of their unique combination of physical, chemical, and electrical properties. Furthermore, the combination of these resins with polyamide resins into compatibilized blends results in additional overall properties such as chemical resistance, high strength, and high flow. Examples of such compatibilized blends can be found in U.S. Patents 4,315,086 (Ueno, et al); 4,659,760 (van der Meer); and 4,732,938 (Grant, et al).

The physical properties of PPE/polyamide blends make them attractive for a variety of end-use articles in the automotive market, especially for various painted exterior components. Some of the more desirable applications, for example, automotive fenders require the molded plastic parts to go through high temperature ovens used to cure the anti-corrosion coating that has been applied to the metal panels. These ovens typically reach temperatures of about 330-400°F or higher for periods of 10 to 50 minutes or longer. The ability to withstand the time and temperature of the ovens without distortion limits the success of many plastic resins. Moreover, paint adhesion issues with plastic panels after passing through the ovens has also limited their acceptance.

It is therefore apparent that a need continues to exist for improved thermoplastic compositions and method to improve paint adhesion on such compositions for painted automotive components.

SUMMARY OF THE INVENTION

The present invention provides methods, compositions, and articles having improved paint adhesion properties. The invention comprises an amount of antioxidant effective to increase the adhesion of paint to an article made from the thermoplastic resin. In a preferred embodiment, the article has been subjected to a temperature of about at least about 330°F for a period of at least about 10 minutes. In a preferred embodiment, the antioxidant, also known as a stabilizer, or mixture of stabilizers is selected from the group consisting of the phenolic antioxidants, the 3-arylbenzofuranones, the hindered amine stabilizers, the ultraviolet light absorbers, the alkaline metal salts of fatty acids, the hydrotalcites, the epoxydized soybean oils, the hydroxylamines, the tertiary amine oxides, thermal reaction products of tertiary amine oxides, the thiosynergists, and mixtures containing at least one of the foregoing.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a boxplot of the relative bond strengths of painted molded articles made from the compositions in Table 1.

Figure 2 is a dotplot of the relative bond strengths of painted molded articles made from the compositions in Table 1.

DETAILED DESCRIPTION OF THE INVENTION

In the practice of a preferred embodiment of the invention, the resin composition comprises a compatibilized blend of a polyphenylene ether resin and a polyamide resin. Compatibilized blends of a polyphenylene ether resin and a polyamide resin are generally known in the art. These blends are typically made through reactive compounding techniques involving addition of a compatibilizing agent to compositions containing polyphenylene ether resin and polyamide resin. The compatibilizing agent is thought to result in reaction products between the polyphenylene ether resin and a polyamide resin and that these reaction products improve the compatibility between the polyphenylene ether resin and polyamide resin. The improved compatibility results in enhanced physical properties such as, for example, increased ductility. Illustrative compatibilizing agents for blends of polyphenylene ether resin and polyamide resin include citric acid, maleic anhydride, fumaric acid, malic acid as well as various derivatives of the foregoing.

The ratio of polyphenylene ether resin to polyamide resin can vary widely but is preferably adjusted so that the polyamide resin remains the continuous phase. Preferably the polyamide is at least about 40% by weight of the total resin composition. Increasing the level of the polyamide results in enhanced ductility and flow and is often preferred. The resin compositions may contain more than one type of polyamide resin such as a blend of nylon 6 and nylon 6,6. Moreover, the amine to acid endgroup ratio of the polyamide resin may also be varied as well as the degree of branching and relative viscosity of the polyamide contained within the resin composition.

The polyphenylene ether resins useful in the present invention include all known polyphenylene ether resins. Preferable resins include poly(2,6-dimethylphenylene ether) as well as the copolymer resins made from 2,6-dimethylphenol and 2,3,6-trimethylphenol. In a preferred embodiment, the polyphenylene ether resin is a high glass transition temperature copolymer resin made from 2,6-dimethylphenol and 2,3,6-trimethylphenol in a monomer weight ratio of between about 1:3 and 3:1, preferably between about 4:6 to 6:4. High glass transition temperature copolymer resins such as the foregoing increase the heat resistance capability of the compatibilized blend of polyphenylene ether resin and polyamide resin as compared to the same composition made utilizing poly(2,6-dimethylphenylene ether) resin. These and other variations of the polyamide and the polyphenylene ether resins do not detract from the present invention.

The present invention also contains an amount of a stabilizer or mixture of stabilizers effective to enhance the paint adhesion characteristics of the composition, wherein the stabilizer or mixture thereof is selected from the group consisting of the phenolic antioxidants, the hindered amine stabilizers, the ultraviolet light absorbers, the alkaline metal salts of fatty acids, the hydroxyl amines, and the thiosynergists.

The phenolic antioxidants useful in the instant compositions embrace a large family of compounds examples of which are given below.

Simple 2,6-dialkylphenol, such as, for example, 2,6-di-tert.-butyl-4-methylphenol, 2-tert.-butyl-4,6-di-methylphenol, 2,6-di-tert.-butyl-4-methoxymethylphenol 2,6-dioctadecyl-4-methylphenol and 2,6-di-tert-butylphenol. Vitamin E and derivatives of vitamin E are also useful phenolic antioxidants.

Derivatives of alkylated hydroquinones, such as for example, 2,5-di-tert.-butyl-hydroquinone, 2,5-di-tert.-amylhydroquinone, 2,6-di-tert.-butyl-hydroquinone, 2,5-di-tert.-butyl-4-hydroxy-anisole, 3,5-di-tert.-butyl4-

hydroxy-anisole, tris-(3,5-di-tert.-butyl4-hydroxyphenyl) phosphite, 3,5-di-tert.-butyl4-hydroxyphenyl stearate and bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

Hydroxylated thiodiphenyl ethers, such as, for example, 2,2'-thio-bis-(6-tert.-butyl-4-methylphenol), 2,2'-thio-bis-(4-octylphenol), 4,4'-thio-bis-(6-tert.-butyl-3-methylphenol), 4,4'-thio-bis-(3,6-di-sec.-amylphenol), 4,4'-thio-bis-(6-tert.-butyl-2-methylphenol) and 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

Alkylidene-bisphenols, such as, for example, 2,2'-methylene-bis-(6-tert.-butyl-4-methylphenol), 2,2'-methylene-bis-(6-tert.-butyl-4-ethylphenol), 4,4'-methylene-bis-(6-tert.-butyl-2-methylphenol), 4,4'-methylene-bis-(2,6-di-tert.-butylphenol), 2,6-di(3,-tert.-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 2,2'-methylene-bis-[4-methyl-6-(alpha -methylcyclohexyl)-phenol], 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)-butane, 1,1-bis-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-butane, 2,2-bis-(3,5-di-tert.-butyl4-hydroxyphenyl)-propane, 1,1,3-tris-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-butane, 2,2-bis-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert.-butyl-4-hydroxy-2-methylphenyl)-pentane and ethylene glycol bis-[3,3-bis-(3-tert.-butyl-4-hydroxyphenyl)-butyrate].

O-, N- and S-benzyl compounds, such as, for example, 3,5,3',5'-tetra-tert.-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzyl-mercaptoacetate, tris-(3,5-di-tert.-butyl-4-hydroxybenzyl)-amine and bis-(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate.

Hydroxybenzylated malonates, such as for example, dioctadecyl 2,2-bis-(3,5-di-tert.-butyl-2-hydroxybenzyl)-malonate, dioctadecyl 2-(3-tert.-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercapto-ethyl 2,2-bis-(3,5-di-tert.-butyl4-hydroxybenzyl)-malonate and di-[4-(1,1,3,3-

tetramethylbutyl)-phenyl]2,2-bis-(3,5-di-tert.-butyl-4- hydroxybenzyl)-malonate.

Hydroxybenzyl-aromatic compounds, such as, for example, 1,3,5-tri-(3,5-di-tert.-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-di-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene and 2,4,6-tri(3,5-di-tert.-butyl-4-hydroxybenzyl)-phenol.

s-Triazine compounds, such as, for example, 2,4-bisoctylmercapto-6-(3,5-di-tert.-butyl-hydroxl-anilino)-s-triazine, 2-octylmercapto,4,6-bis-(3,5-di-tert.-butyl-4-hydroxy anilino)-s-triazine, 2-octylmercapto-4,6-bis-(3,5-di-tert.-butyl-4-hydroxyphenoxy)-s-triazine, 2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenoxy)-s-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenylethyl)-s-triazine, 1,3,5-tris-(2,6-di-methyl-3-hydroxy-4-tert-butylbenzyl)isocyanurate and 1,3-5-tris-(3,5-di-tert.-butyl-4-hydroxybenzyl)isocyanurate.

Amides of beta-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionic acid, such as, for example, 1,3,5-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl-propionyl)-hexahydro-s-triazine and N,N'-di(3,5-di-tert.-butyl-4-hydroxyphenyl-propionyl)-hexamethylenediamine. N,N'-bis-beta-(3,5-di-t-butyl-4-hydroxyphenyl)-propionylhydrazine.

Esters of beta-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, such as, for example with methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, diethylene glycol, thiodiethylene glycol, triethylene glycol, neopentylglycol, pentaerythritol, 3-thia-undecanol, 3-thia-pentadecanol, trimethylhexanediol, trimethylolethane, trimethylolpropane, tris-hydroxyethyl isocyanurate and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

Esters of beta-(5-tert.-butyl-4-hydroxyl-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, such as, for example, with

methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, diethylene glycol, triethylene glycol, thiodiethylene glycol, neopentylglycol, pentaerythritol, 3-thia-undecanol, 3-thia-pentadecanol, trimethylhexanediol, trimethylolethane, trimethylolpropane, tris-hydroxyethyl isocyanurate and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane.

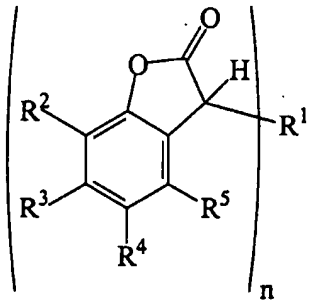
Esters of 3,5-di-tert.-butyl-4-hydroxyphenylacetic acid with monohydric or polyhydric alcohols, such as for example, with methanol, ethanol, octadecanol, 1,6-hexandiol, 1,9-nonanediol, ethylene glycol, 1,2-propenediol, diethylene glycol, thio-diethylene glycol, neopentylglycol, pentaerythritol, 3-thia-undecanol, 3-thia-pentadecanol, trimethylhexanediol trimethylolethane, trimethylolpropane, tris-hydroxyethyl isocyanurate and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]-octane, especially the tetrakis ester of pentaerythritol.

The phenolic antioxidant of particular interest is selected from the group consisting of n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 3,6-dioxaoctamethylene bis(3-methyl-5-tert-butyl-4-hydroxyhydrocinnamate), 2,6-di-tert-butyl-p-cresol, 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 1,3,5-tris(2,6-dimethyl4-tert-butyl-3-hydroxybenzyl)isocyanurate, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-tris[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl]isocyanurate, 3,5-di-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitol, hexamethylene bis(3,5-di-tert-butyl-4-hyroxyhydrocinnamate), 1-(3,5-di-tert-butyl4-hydroxyanilino)-3,5-di(octylthio)-s-triazine, N,N'-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide), calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate), ethylene bis[3,3-di(3-tert-butyl-4-

hydroxyphenyl)butyrate], octyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide, and N,N'-bis-[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl]-oxamide.

A most preferred embodiment has as the phenolic antioxidant, neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), n-octadecyl 3,5-di-tert-butyl4-hydroxyhydrocinnamate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl4-hydroxybenzyl)benzene, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 2,6-di-tert-butyl-p-cresol or 2,2'-ethylidene-bis(4,6-di-tert-butylphenol). In an especially preferred embodiment, the phenolic antioxidant is pentaerythritol tris ester with 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid.

When the present compositions contain a 3-arylbenzofuranone, the 3-arylbenzofuranone is of the formula

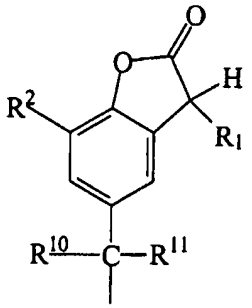


wherein, when n is 1, R^1 is an unsubstituted or substituted carbocyclic or heterocyclic aromatic ring system,

wherein, when n is 2, R^1 is unsubstituted or C_1-C_4alkyl- or hydroxy-substituted phenylene or naphthylene; or is -R^6-X-R^7-, and

wherein R^2, R^3, R^4 and R^5 are each independently of one another hydrogen, chloro, hydroxy, C_1-C_{25}alkyl, C_7-C_9-phenylalkyl, unsubstituted or C_1-C_4alkyl-substituted phenyl, unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl; C_1-C_{18}alkoxy, C_1-C_{18}alkylthio, C_1-C_4alkylamino, di-(C_1-C_4alkyl)amino, C1-

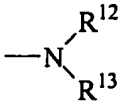
C_{25}alkanoyloxy, C_1-C_{25}alkanoylamino, C_3-C_{25}alkenoyloxy, C_3-C_{25}alkanoyloxy which is interrupted by oxygen, sulfur or > N-R^8; C_6-C_9cycloalkylcarbonyloxy, benzoyloxy or C_1-C_{12}alkyl-substituted benzoyloxy; or each pair of substituents R^2 and R^3 or R^3 and R^4 or R^4 and R^5, together with the linking carbon atoms, forms a benzene ring; R^4 is additionally -$(CH_2)_p$-COR^9 or -$(CH_2)_q$OH, or, if R^3 and R^5 are hydrogen, R^4 is additionally a radical of formula



wherein R^1 is as defined above when n = 1, R^6 and R^7 are each independently of the other unsubstituted or C_1-C_4alkyl-substituted phenylene or naphthylene, R^8 is hydrogen or C_1-C_8alkyl, R^9 is hydroxy,

(-O^- 1/r M^{r+});

C_1-C_{18} alkoxy or



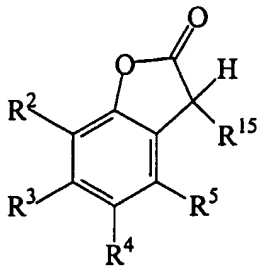
R^{10} and R^{11} are each independently of the other hydrogen, CF_3, C_1-C_{12}alkyl or phenyl, or R^{10} and R^{11}, together with the linking carbon atom, form a C_5-C_8cycloalkylidene ring which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl groups, R^{14} is hydrogen or C_1-C_{18}alkyl, M is a metal cation of valency r, X is a direct bond, oxygen, sulfur or NR^{14},

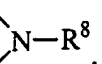
n is 1 or 2,

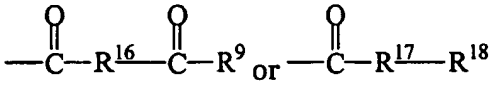
p is 0, 1 or 2,

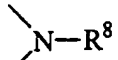
q is 1, 2, 3, 4, 5 or 6, and

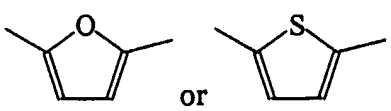
r is 1, 2 or 3, which process comprises reacting a compound of formula



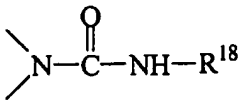
wherein R^{15} is halogen or $-OR'^{15}$, R'^{15} is hydrogen, C_1-C_{25}alkanoyl, C_3-C_{25}alkenoyl, C_3-C_{25}alkanoyl which is interrupted by oxygen, sulfur or  ; C_6-C_9cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1-C_{12}alkyl-substituted benzoyl; naphthoyl or C_1-C_{12}alkyl-substituted naphthoyl; C_1-C_{25}alkanesulfonyl, fluoro-substituted C_1-C_{25}alkanesulfonyl; phenylsulfonyl or C_1-C_{12}alkyl-substituted phenylsulfonyl;



R^{16} is a direct bond, C_1-C_{18}alkylene, C_2-C_{18}alkylene which is interrupted by oxygen, sulfur or  ; C_2-C_{18}alkenylene, C_2-C_{20}alkylidene, C_7-C_{20}phenylalkylidene, C_5-C_8cycloalkylene, C_7-C_8bicycloalkylene, unsubstituted or C_1-C_4alkyl-substituted phenylene,



R^{17} is oxygen, -NH- or



and

R^{18} is C_1-C_{18}alkyl or phenyl, with a compound of formula

$$[H]_n\text{-}R^1.$$

Useful 3-arylbenzofuranones are known compounds and include those found in U.S. Patent Nos. 4,325,863; 4,338,244, 5,175,312, and 5,607,624.

An especially preferred 3-arylbenzofuranone for use in the present invention is 5,7-di-tert-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one.

When the instant compositions contain a thiosynergist, such thiosynergists may be for example dilauryl thiodipropionate, distearyl thiodipropionate or neopentanetetrayl tetrakis(3-dodecylthiopropionate). Distearyl thiodipropionate, dilauryl thiodipropionate, and pentaerythritol betalaurylthiopropionate is particularly preferred.

When the instant compositions contain an alkaline metal salt of a fatty acid, such salts are the alkali metal, alkaline earth metal, zinc, cadmium or aluminum salts of the higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, sodium ricinoleate, or potassium palmitate. Calcium stearate is particularly preferred.

When the instant compositions contain a hindered amine stabilizer, such hindered amines may for example be 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2-6,6-tetramethylpiperidine, bis-(2,2,6,6-tetramethylpiperidyl)sebacate, or 3-n-octyl-7,7,9,9-tetramethyl-1,3,-8-triaza-spiro[4.5]decane-2,4-dione. Amine oxides of hindered amine stabilizers are also included in the present invention.

The hindered amine stabilizers of particular interest are selected from the group consisting of bis(2,2,-6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) (3,5-di-tert-butyl-4-hydroxybenzyl)-butylmalonate, tris(2,2,6,6-tetramethylpiperidin-4-yl) nitrilotriacetate, 1,2-bis(2,2,6,6-tetramethyl-3-oxopiperazin-4-yl)ethane, 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2]heneicosane, polycondensation product of 2,4-dichloro-6-tert-octylamino-s-triazine and 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine), polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, polycondensation product of 4,4'-hexamethylenebis(amino-2,2,6-6-tetramethylpiperidine) and 1,2-dibromoethane, polycondensation product of 2,4-dichloro-6-morpholino-s-triazine and 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine), N,N'N",N"'-tetrakis[(4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amino-s- triazin-2-yl]-1,1 0-diamino-4,7-diazadecane, octamethylene bis(2,2,6,6-tetramethylpiperidin-4-carboxylate), and 4,4'-ethylenebis-(2,2,6,6-tetramethylpiperazin-3-one).

A most preferred embodiment has as the hindered amine stabilizer bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the polycondensation product of 2,4-dichloro-6-tert-octylamino-s-triazine and 4,4'-hexamethylenebis(amino-2,2-6,6-tetramethylpiperidine), or N,N',N",N"'-tetrakis[(4,6-bis(butyl-(2,2,6,6-tetramethyl-piperidin-4-yl)amino)-s -triazine-2-yl]-1,10-diamino-4,7-diazadecane, as well as mixtures of amine stabilizers containing at least one of the foregoing.

When the instant compositions contain an ultraviolet light absorber, such light absorbers may include the 2H-benzotriazoles, the benzophenones, the oxanilides, the alpha-cyanocinnamates the substituted benzoate esters or the nickel salts of the O-alkyl hindered phenolic benzylphosphonates.

Examples of such ultraviolet light absorbers are seen below.

2-(2'-Hydroxyphenyl)-benzotriazoles, e.g., the 5'-methyl-, 3',5'-di-tert.-butyl-, 5'-tert.-butyl-, 5'-(1,1,3,3-tetramethylbutyl)-, 5-chloro-3',5'-di-tert.-butyl-5-chloro-3'-tert.-butyl-5'-methyl-, 3'-sec.-butyl-5'-tert.-butyl-, 3'- alpha -methylbenzyl -5'-methyl, 3'- alpha-methylbenzyl-5'-methyl-5-chloro-, 4'-hydroxy-, 4'-methoxy-, 4'-octoxy-, 3',5'-di-tert.-amyl-, 3'-methyl-5'-carbomethoxyethyl- and 5-chloro-3',5'-di-tert.-amyl-derivative.

2,4-bis-(2'-Hydroxyphenyl)-6-alkyl-s-triazines, e.g., the 6-ethyl-, 6-heptadecyl- or 6-undecyl-derivative.

2-Hydroxybenzophenones e.g., the 4-hydroxy-, 4-methoxy-, 4-octoxy-, 4-decyloxy-, 4-dodecyloxy-, 4-benzyloxy-, 4,2',4'-trihydroxy-, 2,2',4,4'-tetrahydroxy- or 2'-hydroxy-4,4'-dimethoxy-derivative.

1,3-bis-(2'-Hydroxybenzoyl)-benzenes, e.g., 1,3-bis-(2'-hydroxy-4'-hexyloxy-benzoyl)-benzene, 1,3-bis-(2'-hydroxy-4'-octyloxy-benzoyl)-benzene or 1,3-bis-(2'-hydroxy4'-dodecyloxybenzoyl)-benzene.

Esters of optionally substituted benzoic acids, e.g., phenylsalicylate octylphenylsalicylate, dibenzoylresorcin, bis-(4-tert.-butylbenzoyl)-resorcin, benzoylresorcin, 3,5-di-tert.-butyl-4-hydroxybenzoic acid-2,4-di-tert.-butylphenyl ester or -octadecyl ester or -2-methyl-4,6-di-tert.-butyl ester.

Acrylates, e.g., alpha -cyano- beta, beta -diphenylacrylic acid-ethyl ester or isooctyl ester, alpha -carbomethoxy-cinnamic acid methyl ester, alpha -cyano-beta -methyl-p-methoxy-cinnamic acid methyl ester or -butyl ester or N(beta-carbomethoxyvinyl)-2-methyl-indoline.

Oxalic acid diamides, e.g., 4,4'-di-octyloxy-oxanilide, 2,2'-di-octyloxy-5,5'-di-tert.-butyl-oxanilide, 2,2'-di-dodecyloxy-5,5-di-tert.-butyl-oxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis-(3-dimethyl-aminopropyl)-oxalamide, 2-ethoxy-5-tert.-butyl-2'-ethyloxanilide and the mixture thereof with 2-ethoxy-

2'-ethyl-5,4'-di-tert.-butyl-oxanilide, or mixtures of orlho- and para-methoxy- as well as of o- and p-ethoxy-disubstituted oxanilides.

Preferably the ultraviolet light absorber used in the instant compositions is 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole, 2-[2-hydroxy-3,5-di-(alpha,alpha-dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, 2-hydroxy-4-octyloxybenzophenone, nickel bis(O-ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate), 2,4-dihydroxybenzophenone, 2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole, nickel butylamine complex with 2,2'-thiobis(4-tert-butylphenol), 2-ethoxy-2'-ethyloxanilide or 2-ethoxy-2'-ethyl-5,5'-ditert-butyloxanilide.

When the instant compositions contain a hydroxylamine, such hydroxylamines include, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dioctylhydroxylamine, N,N-di-tert-butylhydroxylamine, N-cyclohexylhydroxylamine, N-cyclododecylhydroxylamine, N,N-dicyclohexylhydroxylamine, N,N-dibenzylhydroxylamine, N,N-didecylhydroxylamine, N,N-di(coco alkyl)hydroxylamine, N,N-di(C20-C22 alkyl)hydroxylamine, and N,N-dialkylhydroxylamine derived from hydrogenated tallow amine (i.e., N,N-di(tallow alkyl)hydroxylamine), as well as mixtures containing any of the foregoing. Other useful hydroxylamines are known in the art such as these in U.S. Pat. Nos. 3,644,278; 3,778,464; and 4,590,231.

The compositions of the instant invention may also contain other additives such as the pigments, colorants or dyes, light stabilizers such as metal deactivators, talc and other fillers, etc.

The stabilizer combinations of this invention stabilize polymeric resins especially during high temperature bake cycles with enhanced paint adhesion as compared to the compositions not containing the stabilizer or containing the stabilizer in an amount that is not effective to increase the paint adhesion.

The instant stabilizers may readily be incorporated into the polymeric resins by conventional techniques, at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizer may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension, or emulsion of the polymer. The stabilized compositions of the invention may optionally also contain from about 0.01 to about 5%, preferably from about 0.025 to about 2%, and especially from about 0.1% to about 1%, by weight of various conventional additives, such as the following, or mixtures thereof.

The following may be mentioned as examples of further additives that can be used in the instant compositions.

Metal deactivators, e.g., oxanilide, isophthalic acid dihydrazide, sebacic acid-bis-phenylhydrazide, bis-benzylideneoxalic acid dihydrazide, N,N'-diacetal-adipic acid dihydrazide, N,N'-bis-salicyloyl-oxalic acid dihydrazide, N,N'-bis-salicyloylhydrazine, N,N'-bis-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-hydrazine, N-salicyloyl-N'-salicylalhydrazine, 3-salicyloyl-amino-1,2,4-triazole or N,N'-bis-salicyloyl-thiopropionic acid dihydrazide.

Nucleation agents, e.g., 4-tert.-butylhenzoic acid, adipic acid, diphenylacetic acid or substituted sorbitols such as 1,3; 2,4-dibenzylidenesorbitol.

Other additives that can be incorporated in the stabilized compositions are antiblocking agents, clarifiers, antiozonants, lubricants such as stearyl alcohol, fillers, carbon black, asbestos, kaolin, talc, glass fibers, pigments, optical brighteners, flameproofing agents and antistatic agents.

The compatibilized blend of polyphenylene ether resin and polyamide resin additionally contain various property modifiers such as elastomers for ductility enhancement. Useful elastomers for this purpose are known in the art and include, for example, styrenic block copolymers and various acid functionalized ethylene-propylene copolymers (e.g., EP-graft-maleic anhydride). Especially preferred are the so called elastomeric block copolymers, for example, A-B-A triblock copolymers and A-B diblock copolymers. The A-B and A-B-A type block copolymer rubber additives which may be used are thermoplastic rubbers comprised of one or two alkenyl aromatic blocks which are typically styrene blocks and a rubber block, e.g., a butadiene block which may be partially or totally hydrogenated. Mixtures of these triblock copolymers and diblock copolymers having hydrogenated rubber blocks are especially preferred in the present compositions.

Suitable A-B and A-B-A type block copolymers are disclosed in, for example, U.S. Patent Nos. 3,078,254, 3,402,159, 3,297,793, 3,265,765, and 3,594,452 and U.K. Patent 1,264,741. Examples of typical species of A-B and A-B-A block copolymers include polystyrene-polybutadiene (SBR), polystyrene-poly(ethylene-propylene), polystyrene-polyisoprene, poly(α-methylstyrene)-polybutadiene, polystyrene-polybutadiene-polystyrene (SBR), polystyrene-poly(ethylene-butylene)-polystyrene, polystyrene-polyisoprene-polystyrene and poly(α-methylstyrene)-polybutadiene-poly(α-methylstyrene), as well as the selectively hydrogenated versions thereof. In an preferred embodiment of the present invention, mixtures of the polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene) copolymers are utilized.

Such A-B and A-B-A block copolymers are available commercially from a number of sources, including Phillips Petroleum under the trademark SOLPRENE, Shell Chemical Co., under the trademark KRATON, Dexco under the tradename VECTOR, and Kuraray under the trademark SEPTON.Other

property modifiers include nucleating agents, stabilizers, pigments, dyes, and mineral fillers and reinforcing agents.

Also useful elastomers include functionalized elastomeric polyolefins such as elastomeric polyolefins containing at least one moiety of the group consisting of anhydride, epoxy, oxazoline, and orthoester. The essential structural units of the elastomeric polyolefin are derived from ethylene and at least one C_{3-8} 1-olefin, such as, propylene, 1-butene, 1-hexene, and 1-octene. The proportions of ethylene and at least one C_{3-8} 1-olefin are not critical provided that they together constitute the major portion of the polymer.

A useful amount of the optional elastomeric block copolymers is between about 1% and about 20% by weight, preferably between about 6% and about 15% by weight, wherein the weight percentages are based on the entire weight of the composition.

In a preferred embodiment, the resin composition contains at least one conductive additive. The conductive additive is preferably selected from the group consisting of conductive carbon black, conductive carbon fibers including milled fibers, conductive carbon fibrils, and various mixtures thereof. The conductive additive can be added directly into the compatibilized blend during the melt processing step or preferably, the conductive additive can be pre-dispersed into either the polyphenylene ether resin or the polyamide resin. It is preferable to pre-disperse the conductive additive into the polyamide phase so as to make a concentrate of the conductive additive in the polyamide. In the practice of the invention it is preferred for the conductive material to reside primarily with the polyamide phase as greater conductivity can be achieved with a smaller amount of the conductive additive. It is also possible to use more than one conductive additive concentrate in the preparation of the resin composition.

The electrically conductive carbon black incorporated into the polymer blend preferably has an average particle size between about 10 and 50

nanometers and a pH between about 6.5 and 10, wherein the percent volatile components in the carbon black is preferably less than 2, more preferably between about 0.2 and 1.5. Generally, and preferably, the pore volume (DBP absorption) of the carbon black is between about 150 and 500 cm^3 /100 g. Exemplary of electrically conductive carbon blacks useful in this invention are those such as AKZO Chemicals Ketjenblacks EC-300J or EC-600J, and Columbian Chemicals Company Conductex 975U and CONDUCTEX SC, and PRINTEX XE 2 from Degussa Corporation.

Useful carbon fibrils include these having diameters between about 3.5 and 500 nanometers such as those obtained from Hyperion Catalyst Company.

The amount of conductive material added is preferably an amount that will result in a final resin composition having a specific volume resistively below 1 x 10^5 Ohm-cm, preferably below 9 x 10^4 Ohm-cm, and having a surface resistance above 1 x 10^5 Ohm, preferably above 1 x 10^6 Ohm. More preferably, the resin composition has a specific volume resistively below 4 x 10^5 Ohm-cm and has a surface resistance above 3.5 x 10^5 Ohm. When the specific volume resistivity is below 10^4 Ohm-cm, the resin composition is sufficiently conductive to allow to electrostatic painting. Conversely, when the surface resistance is above 10^5 Ohm, the resin composition is not so conductive as to have electro-deposition of the corrosion inhibitor onto the plastic component, an undesirable affect. The range of conductive additive does vary depending on a number of factors such as the type of conductive additive and the ratio of polyphenylene ether resin to polyamide resin and the degree of dispersion of the conductive additive.

The range of conductive additive is generally between about 0.4% by weight and about 6% by weight, preferably between about 0.7% by weight and about 2.5% by weight based on the entire weight of the resin composition. Typically, when the resin composition comprises a conductive carbon black powder, it is present in an amount between about 0.8% by weight and about 2.3% by weight, preferably between about 1% by weight and about 2% by

weight, all based on the entire weight of the resin composition. Also, when typically the resin composition comprises a conductive carbon fibril, it is present in an amount between about 0.5% by weight and about 5% by weight, preferably between about 0.7% by weight and about 2.0% by weight, all based on the entire weight of the resin composition. It is within the ability of one of skill in this art to determine a more precise amount of conductive additive required based on the desired degree on conductivity required for a particular application and the resin composition.

The preparation of the compositions of the present invention is normally achieved by merely blending the ingredients under conditions for the formation of an intimate blend. Such conditions often include mixing in single or twin screw type extruders or similar mixing devices that can apply a shear to the components.

All of the ingredients may be added initially to the processing system, or else certain additives may be precompounded with one or more of the primary components, preferably the PPE, the elastomers, and/or the polyamide. It appears that certain properties, such as impact strength and elongation, are sometimes enhanced by initially precompounding the PPE, elastomeric copolymers, optionally with any other ingredients, prior to compounding with the polyamide resin, however, these improvements are done at the expense of increasing the viscosity of the compatibilized composition. While separate extruders may be used in the processing, these compositions are preferably prepared by using a single extruder having multiple feed ports along its length to accommodate the addition of the various components. It is often advantageous to apply a vacuum to the melt through at least one or more vent ports in the extruder to remove volatile impurities in the composition. Those of ordinary skill in the art will be able to adjust blending times and temperatures, as well as component addition, without undue additional experimentation.

It should be clear that methods to make the compositions and articles made from the compositions as disclosed are within the scope of the invention.

The following illustrative examples demonstrate various embodiments of the present invention. However, they are not intended to limit the invention in any manner.

Examples:

A. Blend Formulation

The base composition used in Table 1 contained the following components as parts by weight wherein the total blend formulation by parts by weight is 99.70 phr. All parts are parts by weight per hundred parts resin (phr).

38.44 PPE (poly(2,6-dimethylphenylene ether) having an intrinsic viscosity of about 0.40 as measured in chloroform at 30°C)

44 nylon 6,6

7 Kraton G1651 (S-EB-S triblock copolymer)

3.5 Kraton G1701X (S-EP diblock copolymer)

0.65 citric acid

0.10 KI added as an aqueous solution

0.01 CuI

6.0 carbon fibril master batch (20 weight % fibril having a diameter between about 10 to 30 nanometers + 80 weight % nylon 6,6) as the basic matrix formulation.

The illustrative stabilizers used in Table 1 are as follows:

Irganox 1010: Pentaerythritol tris ester with 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid, chemical abstract service number [84633-54-5]

Seenox 412S: Pentaerythritol betalaurylthiopropionate, chemical abstract service number [29598-76-3]

B. Extrusion (compounding)

Blend formulations were compounded using a WP 53mm TSE using temperature profile of 400-500-600-600-600-600-600-600-600-600-550°F (Zone1-10 plus die), 300 rpm @ 220 lbs/hr run rate.

C. Molding

Molding plaques used for paint adhesion study was 4 in. x12 in. x 1/8 in. molded using a Toshiba ISE310 press at set temperature of 570° and a tool temperature of 170°F.

D. Paint Adhesion Test

The paint adhesion test method and the evaluation criteria used were specifically developed by GE Plastic Coating Laboratory in Louisville, KY.

D1. Sample Preparation

Three replicate 4 in. x12 in. x 1/8 in. plaques of each material are wiped with isopropyl alcohol and dried with lint free cheesecloth to provide a clean surface. Panels are baked by a gas oven at 400°F for 40 minutes to simulate a typical e-coat production heat history. Primer/surfacer (PPG - FCP 6534 - Titanium Frost polyester/urethane, 67% solids primer/surfacer before reduction) is reduced (or diluted) per the paint manufacturer's instructions and applied to the plaques with a Spraymation precision applicator. Applicator is adjusted to deposit 1.2 to 1.4 mils dry film thickness in two (2) passes of atomized paint spray. Painted plaques are baked for thirty (30)

minutes at 320°F per manufacturer's guidelines to cure the primer/surfacer. Cooled plaques are tested for peel adhesion at the top, bottom and middle of each of the three (3) plaques for a total of nine (9) data points per material. A control material with known acceptable performance is always included as a verification point in each study.

D2. Paint Adhesion Test

A ½-inch square of primer/surfacer wiped with isopropyl alcohol to remove dust and oils. One drop of adhesive (Elmer's Wonderbond Plus, manufactured by Borden Chemical, Inc.) is applied to the target area, and one end of a prepared polycarbonate film strip applied with firm pressure. After the adhesive has cured according to its manufacturer's recommendations, a force gauge is clamped to the free end of the polycarbonate strip. The force gauge, calibrated and verified to at least ±0.4 foot-pounds, is pulled by hand at a constant angle until the strip is detached. The value on the force gauge is recorded as Relative Bond Strength (RBS) in unit of ft-lb/0.5 inch, and the failure method evaluated.

D3. Pass/Fail Criteria

The primary constraint for evaluating paint adhesion is a qualitative comparison to a material with known adhesion performance at multiple customers. Quantitative evaluation is limited, but historical data demonstrates that a force of two (2) ft·lb/0.5 inch is recommended and a force of three (3) ft·lb/0.5 inch is desired. This Relative Bond Strength (RBS) has historically been adequate in screening materials that will pass automotive OEM paint adhesion standards. If RBS is below the 3 ft·lb/½-inch, a cohesive failure mode (breakage within the primer/surfacer or the polymer) is preferable to adhesive failure mode (primer/surfacer cleanly removed from the polymer surface).

Results:

Table 1 summarizes a series of experiments illustrating an embodiment of the invention of this disclosure. The conductive formulation 467-8 is typical for exterior body panel applications for online painting capability due to overall balance of its conductivity, high heat resistance and other physical property profile. However, it may not be appropriate for some automotive manufacturers due to its low performance in paint adhesion as judged by Relative Bond Strength (RBS) and the failure mode after peeling test. Samples 467-9 , -5, -4, -6, and -1 are five different blends adding with various type and/or loading of anti-oxidant packages to resolve those shortcomings seen in the control blend. No appreciable improvement is noted at 0.3 phr of Irganox 1010 or Seenox 412S but a large, unexpected improvement is seen at 0.6 phr of Irganox 1010 or Seenox 412S and their combination at 0.3 phr/0.3 phr.

Table 1.

	Control	Examples				
Sample ID	467-8	467-9	467-5	467-4	467-6	467-1
Irganox	0	0	0	0.3	0.6	0.3
Seenox	0	0.3	0.6	0	0	0.3
Plaque 1 -	1.5	2.4	6.2	1.0	7.3	6.9
Plaque 1 -	1.8	1.5	0.9	0.9	7.0	5.7
Plaque 1 -	1.4	4.1	8.5	4.7	8.8	4.6
Plaque 2 -	1.8	0.8	7.4	0.9	7.6	8.0
Plaque 2 -	0.8	0.9	7.7	1.0	8.4	7.3
Plaque 2 -	2.2	0.8	7.8	2.7	7.3	7.0
Plaque 3 -	7.1	1.1	7.1	2.5	4.5	6.9
Plaque 3 -	2.1	2.5	1.5	1.8	6.8	8.1
Plaque 3 -	4.9	1.7	5.8	4.4	4.8	7.1
Relative Bond Strength (ft-lb/0.5 in) -	2.6	1.8	5.9	2.2	6.9	6.8
Relative Bond Strength (ft-lb/0.5 in) -	2.0	1.1	2.8	1.5	1.5	1.1
Failure Mode After	A	A	C	A	C	C
Vicat Softing Temp	394.5	386.6	383.3	388.3	388.6	380.1

A : Adhesive failure
C : Cohesive failure

The RBS data plotted in Figures 1 and 2 demonstrate that 0.6 phr Irganox 1010 and 0.3 phr I-1010/0.3 phr Seenox 412S are better than 0.6 phr Seenox 412S as judged by the mean value and standard deviation (or data distribution).

Heat resistance is another important physical property often necessary for online painting which determines the operation safety margin in high

temperature online painting process (to prevent potential warpage or heat sag of plastic components). Addition of an antioxident (AO) generally lowers the heat resistance of control blend as judged by Vicat Softening temperature. Unexpectedly, blends containing Irganox 1010 exhibit the least deterioration (comparatively) vs counterparts containing Seenox 412S or Irganox 1010/Seenox 412S at same loading.

WHAT IS CLAIMED IS:

1. A method to increase the paint adhesion of an article made from a thermoplastic resin composition, wherein said method comprises:

(a) a thermoplastic resin, and

(b) an amount of at least one antioxidant effective to increase the adhesion of paint to the thermoplastic resin.

2. The method of claim 1, wherein the thermoplastic resin comprises a polyamide resin.

3. The method of claim 1, wherein the thermoplastic resin comprises a compatibilized poly(phenylene ether)-polyamide resin composition.

4. The method of claim 1, wherein the thermoplastic resin comprises a conductivity enhancing agent.

5. The method of claim 1, wherein the thermoplastic resin comprises at least one impact modifier.

6. The method of claim 5, wherein at least one impact modifier is selected from styrenic block copolymers and acid functionalized ethylene-propylene copolymers.

7. The method of claim 1, wherein the thermoplastic resin comprises at least one of polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene).

8. The method of claim 1, wherein the antioxidant is selected from the group consisting of the phenolic antioxidants, the 3-arylbenzofuranones, the hindered amine stabilizers, the ultraviolet light absorbers, the alkaline metal salts of fatty acids, the hydrotalcites, the epoxydized soybean oils, the hydroxylamines, the tertiary amine oxides, thermal reaction products of

tertiary amine oxides, the thiosynergists, and mixtures containing at least one of the foregoing.

9. The method of claim 1, wherein the antioxidant is selected from the group consisting of hindered phenols, thioesters, and mixtures comprising at least one of hindered phenols and thioesters.

10. The method of claim 1, wherein the antioxidant is admixed with the thermoplastic resin.

11. The method of claim 1, wherein the antioxidant is present in an amount of at least 0.1% by weight based upon the total weight of the thermoplastic resin composition.

12. The method of claim 1, wherein the thermoplastic resin composition has a Vicat softening temperature that is at least 90% of the Vicat softening temperature of the same thermoplastic resin composition not containing the antioxidant.

13. The method of claim 1, wherein the paint adhesion failure is at least partially cohesive.

14. The method of claim 1, wherein the relative bond strength of paint to the article is at least 1 ft-lb/ 0.5 inch.

15. The method of claim 1, wherein the antioxidant is at least one of pentaerythritol tris ester with 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid and pentaerythrital betalaurylthiopropionate.

16. An article comprising:

(a) a thermoplastic resin, and

(b) an amount of antioxidant effective to increase the adhesion of paint to an article made from the thermoplastic resin.

17. The article of claim 16, wherein the thermoplastic resin comprises a compatibilized poly(phenylene ether)-polyamide resin composition.

18. The article of claim 16, wherein the thermoplastic resin comprises a conductivity enhancing agent.

19. The article of claim 16, wherein the thermoplastic resin comprises at least one impact modifier.

20. The article of claim 19, wherein at least one impact modifier is selected from styrenic block copolymers and acid functionalized ethylene-propylene copolymers.

21. The article of claim 16, wherein the thermoplastic resin comprises at least one of polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene).

22. The article of claim 16, wherein the antioxidant is selected from the group consisting of the phenolic antioxidants, the 3-arylbenzofuranones, the hindered amine stabilizers, the ultraviolet light absorbers, the alkaline metal salts of fatty acids, the hydrotalcites, the epoxydized soybean oils, the hydroxylamines, the tertiary amine oxides, thermal reaction products of tertiary amine oxides, the thiosynergists, and mixtures containing at least one of the foregoing.

23. The article of claim 16, wherein the antioxidant is selected from the group consisting of hindered phenols, thioesters, and mixtures comprising at least one of hindered phenols and thioesters.

24. The article of claim 16, wherein the antioxidant is admixed with the thermoplastic resin.

25. The article of claim 16, wherein the antioxidant is present in an amount of at least 0.1% by weight based upon the total weight of the thermoplastic resin composition.

26. The article of claim 16, wherein the thermoplastic resin composition has a Vicat softening temperature that is at least 90% of the Vicat softening temperature of the same thermoplastic resin composition not containing the antioxidant.

27. The article of claim 16, wherein paint adhesion failure of paint to the article is at least partially cohesive.

28. The article of claim 16, wherein the relative bond strength of paint to the article is at least 1 ft-lb/ 0.5 inch.

29. The article of claim 16, wherein the antioxidant is at least one of pentaerythritol tris ester with 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid and pentaerythrital betalaurylthiopropionate.

30. The article of claim 16, wherein the article is an exterior automotive article.

31. An article comprising:

(a) a thermoplastic resin, and

(b) an amount of antioxidant effective to increase the adhesion of paint to an article made from the thermoplastic resin, wherein the article has been subjected to a temperature of at least about 330°F for period of at least about 10 minutes.

32. An article consisting essentially of:

(a) a compatibilized poly(phenylene ether)-polyamide resin composition,

(b) at least one of polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene),

(c) a conductivity enhancing agent, and

(d) an amount of antioxidant effective to increase the adhesion of paint to article.

33. A resin composition comprising:

(a) a thermoplastic resin, and

(b) an amount of antioxidant effective to increase the adhesion of paint to an article made from the thermoplastic resin.

34. A composition comprising:

(a) a compatibilized poly(phenylene ether)-polyamide resin composition,

(b) at least one of polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene),

(c) a conductivity enhancing agent, and

(d) an amount of antioxidant effective to increase the adhesion of paint to an article made from the composition.

35. A composition consisting essentially of:

(a) a compatibilized poly(phenylene ether)-polyamide resin composition,

(b) at least one of polystyrene-poly(ethylene-butylene)-polystyrene and polystyrene-poly(ethylene-propylene),

(c) a conductivity enhancing agent, and

(d) an amount of antioxidant effective to increase the adhesion of paint to an article made from the composition.

Figure 1.

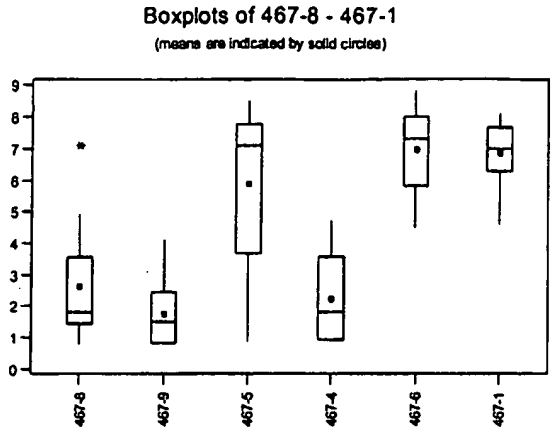
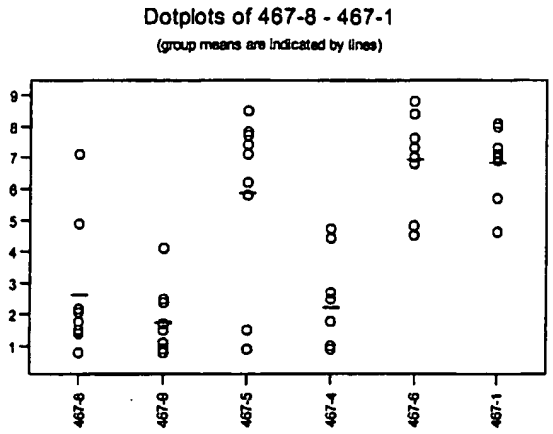

Boxplots of 467-8 - 467-1
(means are indicated by solid circles)
9
8
7
6
5
4
3
2
1
0
467-8
467-9
467-5
467-4
467-6
467-1

Figure 2.


Dotplots of 467-8 - 467-1
(group means are indicated by lines)
9
8
7
6
5
4
3
2
1
467-8
467-8
467-5
467-4
467-6
467-1

INTERNATIONAL SEARCH REPORT

Internati ılication No
PCT/US 01/40377

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L71/12 C08L77/00 C08K5/00 C08J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 674 928 A (CHISHOLM ET AL) 7 October 1997 (1997-10-07) column 1, line 51 - line 53 column 2, line 5 - line 6 claim 1; table III ---	1,8-12, 15,16, 22-25,30
X	EP 0 248 526 A (MITSUBISHI PETROCHEMICAL CO) 9 December 1987 (1987-12-09) page 2, line 2 page 6, line 25 page 13, paragraph 4 - paragraph 5 claims 1,3,5,6,9,10; examples; tables --- -/--	1-3,5, 8-11, 15-17, 19, 22-25,33

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 2001	15/10/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Engel, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 394 055 A (SUMITOMO CHEMICAL CO) 24 October 1990 (1990-10-24) page 8, line 11 - line 14; examples -----	1-3,5,6, 16,30

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INTERNATIONAL SEARCH REPORT

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		JP 3014870 A	23-01-1991
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